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First Annual Technical Summary Report

November 1, 1961 to October 31, 1962

INVESTIGATION OF THE CHARACTERISTICS OF INTERMETALLIC
COMPOUNDS AS THERMIONIC EMITTERS

Prepared for

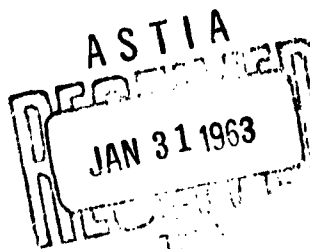Office of Naval Research
Power Branch

Contract NONR-3361(01)

Project No. NR 099-362

Submitted by

University of Denver
Denver Research Institute

December 31, 1962

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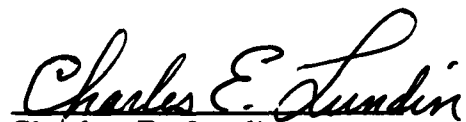
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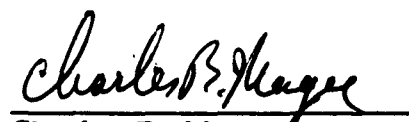Project No. NR 099-362

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ABSTRACT

Equipment has been designed and fabricated for the determination of evaporation rates of intermetallic compounds by means of the Langmuir free evaporation technique. Evaporation rate data have been obtained in the temperature range from 900 to 1200°C for metallic beryllium and for $ZrBe_{13}$, $NbBe_{12}$, and Nb_2Be_{17}. Assuming the evaporating species to be monatomic beryllium, vapor pressures have been calculated from evaporation rates and Van't Hoff plots have been made. The standard enthalpies of sublimation, ΔH_T^0, in kilocalories per gram atom beryllium determined from these plots are: for Be, 79.0; for $ZrBe_{13}$, 85.0; for $NbBe_{12}$, 19.9 and 59.5; and for Nb_2Be_{17}, 98.0 and 55.8. That there are two enthalpies of sublimation for the niobium beryllides may possibly be due to the existence of a heretofore unknown niobium beryllide intermediate in beryllium content between Nb_2Be_{17} and $NbBe_3$. It is possible that both $NbBe_{12}$ and Nb_2Be_{17} decompose upon evaporation to the intermediate species which in turn decomposes to $NbBe_3$.

A high vacuum diode for the determination of the thermionic emission parameters of intermetallic compounds has been designed and constructed. A second diode incorporating many improvements over the first design is now being constructed. Fabrication of cylindrical emitter specimens of $ZrBe_{13}$ has been attempted by a number of techniques. Moderate success has been achieved only by cold pressing followed by sintering.

Apparatus for the determination of the compatibility of intermetallic compounds with cesium vapor has been designed and is now being constructed.

TABLE OF CONTENTS

DENVER RESEARCH INSTITUTE — UNIVERSITY OF DENVER

LIST OF ILLUSTRATIONS

I.   INTRODUCTION

Many advances have been made over the past few years towards the ultimate, practical thermionic conversion of heat into electrical energy. Not the least of these advances has been the improved understanding of the influence that such material properties as crystal structure, crystallite orientation, and electronic states have on the observed thermionic properties of emitter materials. This better understanding has resulted not only from the continued fundamental study of the more or less traditional refractory metal emitters, but also from investigations of less conventional emitter materials such as borides, carbides, and the like. One very large class of materials that have, up to now, received no consideration in this respect are the intermetallic compounds. The very existence of these compounds depends upon those same factors that influence thermionic properties, that is, the chemical bonding characteristics of the component elements and the spatial orientation of these elements in the crystal lattice. These compounds, then, are worthy of study with the assurance that the results will be fruitful from a theoretical standpoint and with the possibility that an emitter material (or materials) of practical value may be developed.

That there are a large number of intermetallic compounds of potential interest is evident from the list presented in Appendix A. In Appendix A only those compounds which melt (or are expected to melt) at temperatures above 1200 °C are listed. In addition to melting points, the crystal structures of the compounds (where known) are given. Very often the melting point and the crystal structure are the only physical properties of intermetallic compounds that are known. This is quite natural since in phase equilibrium studies these are the properties most often used to determine whether or not intermetallic compounds exist.

One group of intermetallic compounds that has elicited considerable interest of late is that comprising the transition metal beryllides. As will be noted in Appendix A, there are a large number of these intermetallic compounds. The high beryllium content beryllides of zirconium ($ZrBe_{13}$ and Zr_2Be_{17}), of niobium ($NbBe_{12}$ and Nb_2Be_{17}), and of tantalum ($TaBe_{12}$ and Ta_2Be_{17}) are of interest as potential nuclear reactor materials. This interest results from the refractory nature of these materials, their resistance to oxidation*, and their high beryllium contents. Because of the intent eventually to couple thermionic conversion

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* While oxidation resistant at temperatures of the order of 1000 °C and above, most, if not all, of these beryllides are attacked by oxygen at lower temperatures. This phenomenon is known as the pest effect.

with a nuclear reactor power source, and because of the experience
that persons in the Metallurgy Division of the Denver Research Institute
have had with beryllides, these materials were selected as the first
group to be studied in this research program.

In any evaluation of materials for use as thermionic emitters
the properties of first concern are, of course, the emission properties,
work function and emission constant. Considering the long life required
for a practical thermionic converter and the possibly deleterious effects
of vapor deposition on relatively cool parts of the cell, another property
of immediate concern is the evaporation-rate as a function of tempera-
ture. Finally in converters utilizing cesium vapor in the interelectrode
space, resistance to cesium vapor attack is an obvious requirement for
the emitter material. These properties: thermionic properties, evap-
oration rates, and compatability with cesium, are being determined for
groups of intermetallic compounds, beginning with the beryllides, in
this research program. The intent is not to survey a large number of
materials in a prefunctory manner. Rather, it is to investigate each
aspect thoroughly seeking interrelationships and correlations between
materials and between the properties of these materials. In this manner
it is hoped that this study will help to better the understanding of the re-
lationship of the chemical nature of the elements to their solid state be-
havior.

This research program was started in November of 1961. This
report covers the work accomplished in the first year's contract period.
The next section summarizes these accomplishments and the following
sections describe the work in some detail. Where appropriate in these
sections the work to be carried out in the next contract period is de-
scribed.

II.   SUMMARY

A.   Evaporation Rate Studies

Equipment has been designed and fabricated for the measurement of evaporation rates by the Langmuir free evaporation technique. Evaporation rate measurements over the temperature range from 900 to 1200°C have been made for beryllium metal and the following beryllides: $ZrBe_{13}$, $NbBe_{12}$, and Nb_2Be_{17}. Representative results are listed below where the evaporation rates at 1000°C are given in milligrams per square centimeter per day:

Material	Evaporation Rate (milligrams/cm²/day)
Be	51.6
$ZrBe_{13}$	12.0
$NbBe_{12}$	10.4
Nb_2Be_{17}	5.9

It will be noted that even though the evaporation rates for the three beryllides are considerably lower than that of beryllium metal, they are still appreciable at this temperature.

X-ray diffraction analyses of the surfaces of the heat shields that surround the specimens during evaporation rate experiments indicate that the evaporating species most probably is, in all cases, beryllium. X-ray diffraction analyses of the surfaces of the beryllide specimens following evaporation rate experiments show the presence of beryllides lower in beryllium content than the original specimen. This implies that the lower beryllium content beryllides are more stable towards evaporation in this temperature range than the higher beryllium content beryllides. For this reason the lower beryllium content beryllides will be studied during the next contract period.

Under the assumption that the evaporating species is, in all cases, monatomic beryllium, measured evaporation rates have been converted to equilibrium decomposition vapor pressures. Van't Hoff plots (logarithm pressure vs. reciprocal absolute temperature) of these data give straight lines the slopes of which are directly related to the standard enthalpies of sublimation, ΔH_T^0, of the evaporating substance

over the temperature range of measurement. The Van't Hoff plots are presented in the body of the report; the enthalpies of sublimation taken from these plots are given below:

Material	ΔH_T^0 (kcal/gram atom beryllium)
Be metal	79. 0
$ZrBe_{13}$	85. 0
$NbBe_{12}$ (fast)	19. 9
$NbBe_{12}$ (slow)	59. 5
Nb_2Be_{17} (fast)	98. 0
Nb_2Be_{17} (slow)	55. 8

It will be noted that for $NbBe_{12}$ and $NbBe_{17}$ two different values are given. This reflects the fact that the evaporation rates were observed to change in the course of the experiments. These data have yet to be confirmed, but assuming that the observations are real, a possible explanation is as follows: In the case of both $NbBe_{12}$ and Nb_2Be_{17} the species present on the surface following the experiments was predominantly $NbBe_3$. Also in both cases an unidentified species was found to be present (following the experiments) in significant amounts. This unidentified species is presumed to be a niobium beryllide with beryllium content intermediate between Nb_2Be_{17} and $NbBe_3$. It is assumed that the slow reaction in both cases (note that the heats of sublimation are very close in magnitude) is the same, that is, the reaction is the decomposition of the unidentified species to $NbBe_3$ and beryllium. The two fast reactions are, then, the decomposition of, in one case, $NbBe_{12}$ to the intermediate species and beryllium, and, in the other case, Nb_2Be_{17} to the intermediate phase and beryllium. Whether or not this hypothesis for the behavior of the niobium beryllides is correct will be determined in forthcoming experiments.

B.   Thermionic Emission Studies

A high vacuum diode for the determination of thermionic emission parameters of intermetallic compounds (beginning with the beryllides) has been designed and constructed. All of the necessary high vacuum equipment and auxiliary electrical equipment have been procured. This first diode has proved to be extremely fragile and it has been virtually impossible to maintain it in a leak free condition. Consequently

a second diode has been designed and is under construction. This second diode incorporates many improvements over the first one and should prove to be sturdy, easy to work with, and easy to keep vacuum tight.

Considerable effort has been devoted to the fabrication of cylindrical specimens of beryllides to be used as emitters in the diode mentioned above. A number of fabrication techniques including isostatic pressing, extrusion, and slip casting, have been attempted without success. Of the techniques which can be carried out in the Metallurgy Department, cold pressing followed by sintering is the one most likely to produce suitable specimens. Because of the success achieved elsewhere in the hot pressing and subsequent grinding of various sized beryllide specimens, consideration is being given to having specimens made by another organization for use in this program. However, since it is most likely that specimens of all the beryllides of interest cannot be obtained from outside sources, cold pressing and sintering operations have been continued. This technique is being refined and will be used for the preparation of specimens of the low beryllium content beryllides.

III.   EVAPORATION RATE STUDIES

At the outset of the research program it was decided to use the Langmuir free evaporation technique for determining the evaporation rates of intermetallic compounds as a function of temperature. This technique, compared to other often used methods such as the Knudsen effusion and transpiration techniques, more closely resembles the conditions under which an emitter is used in practice. In converting evaporation rates determined by the Langmuir technique to vapor pressures, it must be assumed that none of the material that evaporates returns to the sample. If this is not a valid assumption the vapor pressures so determined are not correct. However, the evaporation rates (weight lost per cm^2 per second) as measured are meaningful and can be used to calculate the expected weight loss for a potential emitter as a function of time and temperature. In most other vapor pressure measuring techniques the evaporation rate is not determined directly but must be calculated from the vapor pressure. Hence, if the assumptions necessary to determine vapor pressures are not valid, the computed evaporation rates are incorrect. Thus, the Langmuir technique is the one best suited to the purpose of this research program.

The apparatus was designed and constructed during the first months of the contract period. Many difficulties were encountered in attaining the required high vacuum. These difficulties were eventually overcome and evaporation rate data for some of the beryllide compounds were obtained. The equipment, the test procedures, and the results obtained are described below.

A.   Evaporation Rate Measuring Apparatus

The apparatus consists of a large vacuum chamber in which are enclosed an Ainsworth analytical balance and a resistance heating furnace to heat the samples to the desired temperature. Figure I is a photograph of the exterior of the apparatus and auxiliary equipment. The furnace chamber can be seen suspended (on the left) from the base plate upon which the bell jar and its shield rest. The heating element is a tungsten coil made of three strand wire with a total diameter of 55 mils. The coil is approximately 1 in. in diameter and 1-1/2 in. long, and consists of 6 or 7 loops. Surrounding the coil is a three-ply tantalum heat-shield. The heat-shield rests on a tantalum tripod. Heat flow from the heat-shield is minimized by a knife edge contact to the tripod. The entire
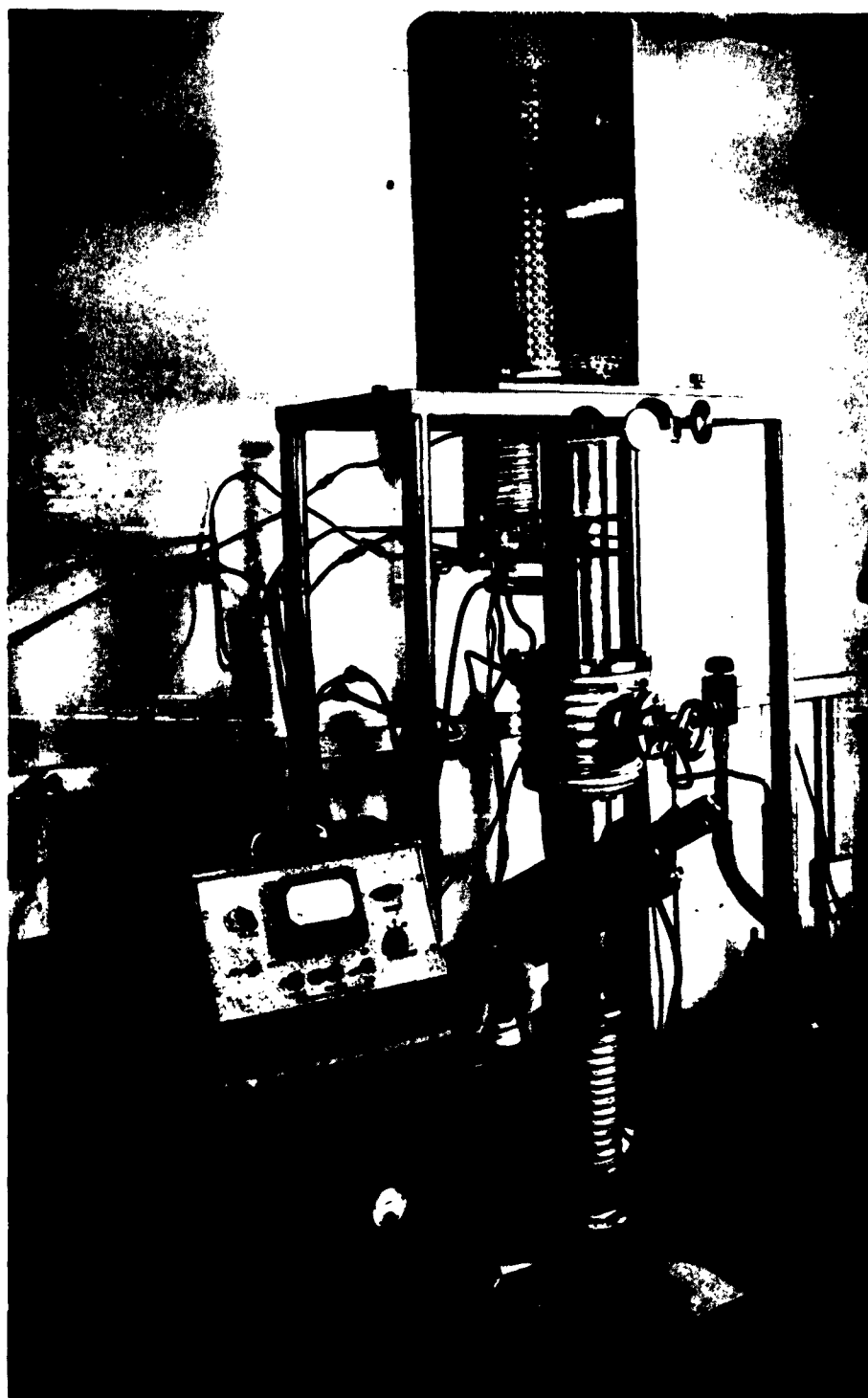
Figure I. Langmuir Type Evaporation Rate Measuring Apparatus and
Auxiliary Equipment

furnace chamber is water cooled. The specimen being studied is suspended from the left-hand pan of the balance such that it is in the center of the tungsten coil.

Power is supplied to the coil by extending the coil wires through the heat shield to terminals in the bottom of the furnace chamber which are connected to the outside power source. The coil wire is insulated from the heat shields by alumina tubing. Power is obtained initially from a 220 volt source. The current is increased by means of two transformers connected in series. A relay allows a third transformer to enter the circuit when the controller calls for more heat. At the present time, a maximum of 46 amps can be obtained. This corresponds to a sample temperature of about 1200°C. New transformers are now being installed which will supply more power to the coil.

Two Pt-Pt 13% Rh thermocouples are located just below the specimen. One of the thermocouples is connected to a potentiometer which measures the temperature; the second, is connected to a Leeds & Northrup controller. The temperature variation during an evaporation study can be kept to less than 5°C.

The analytical balance is an Ainsworth LCB which was modified to operate in a closed vacuum system. The balance is fixed to a 1 in. thick aluminum plate. The balance is leveled by leveling screws between the plate and the frame. A series of gears and O-ring seals allow the pan release and the chain weight to be operated outside the system. A tungsten rod connected to the specimen is attached to the left-hand balance pan. After connecting the sample to the tungsten rod, the sample assembly and the weight of the chain are balanced by weights in the opposite pan. This allows for a 100 mg weight loss from the sample before the system has to be opened. The entire balance is enclosed within a bell jar resting on the aluminum plate.

A series of valves (as may be seen in Figure 1) permit the diffusion pump to operate while the rest of the system is open to the air. The same series of values is used to isolate the diffusion pump such that the forepump may be used as a roughing pump. A vacuum of roughly 10^{-2} mm. of Hg is established before the system is opened to the diffusion pump. With the use of the cold trap (between the diffusion pump and the large valve in Figure 1) an ultimate vacuum of 1×10^{-5} mm. of Hg can be obtained. It was expected that a higher vacuum than this would be achieved. However, considering the size of the system and

the many seals between component parts, 1×10^{-5} mm. of Hg is, perhaps, the limit of the system. This vacuum is sufficient for the experimental measurements of evaporation rates being carried out.

B.   Test Specimens

The beryllide specimens used so far in the program were prepared by the Brush Beryllium Company. These specimens were available through another research program concerning beryllides being carried out by the Metallurgy Division. The specimens, measuring 1/2 in. by 1/2 in. by 1/4 in. , were cut from hot pressed billets and then ground to size to remove surface imperfections and areas of beryllium depletion. Prior to each evaporation study the specimens are cleaned with concentrated phosphoric acid and then washed in water and reagent grade acetone.

C.   Test Procedures

The surface area of the specimen to be studied is accurately measured. Then the specimen, cleaned as described above, is wrapped with 5 mil tungsten wire (two strands at 90° to each other). This wire is attached to the tungsten rod which is in turn attached to the balance pan. The specimen is suspended in such a way that it is in the center of the heating coil and neither it nor the suspending rod touch any parts of the coil, heat shields, or thermocouples. The alignment procedure is very ticklish and a number of runs have been voided because of misalignment.

When the specimen is properly aligned the temperature is raised to the desired value. The weight of the sample is determined as a function of time and the weight loss computed in grams/cm^2/sec. When sufficient data have been obtained at this temperature the temperature is changed to another predetermined value and the weight loss measurements repeated. When the run is completed the X-ray diffraction pattern of the specimen is obtained to determine what material remains on the surface following evaporation. In addition, analysis is made of the material deposited on the heat shields surrounding the specimen in order to help ascertain the species that has evaporated.

D. Results

1-) Beryllium Metal

The first evaporation rate experiments were carried out using pure beryllium metal. The reason for using beryllium was twofold: first, the data obtained could be checked against that reported by other investigators, and secondly, the results would be helpful in interpreting the data obtained for the beryllides.

The temperatures at which measurements were made were 950, 1000, 1050, and 1100°C. At all temperatures the weight loss was found to be linear with time. Weight loss per cm^2 per second was converted to vapor pressure by means of the Langmuir equation: $p = w(2\pi RT/M)^{\frac{1}{2}}$, where p is the vapor pressure, w is the weight loss in grams per cm^2 per second, R is the gas constant, T is the absolute temperature and M is the molecular weight of the evaporating species. It was assumed that the species evaporating from the surface of the beryllium metal was monatomic beryllium.

The results obtained for the metal are summarized below:

Temp. (°C)	Evaporation rate (g/cm²-sec)	Vapor pressure (atmospheres)
950	1.41×10^{-7}	3.70×10^{-8}
1000	5.09×10^{-7}	1.365×10^{-7}
1000	9.84×10^{-7}	3.03×10^{-7}
1050	2.25×10^{-6}	6.15×10^{-7}
1100	4.84×10^{-6}	1.345×10^{-6}

The above vapor pressure data are in substantial agreement with the data of Holden, Speiser and Johnston* over the same temperature range. A Van't Hoff plot (log p vs 1/T) of the above data gives a straight line. The heat of sublimation for Be metal calculated from the slope of this line is 79.0 Kcal/mole. The heat of sublimation reported by Holden, et al., is 76.36 Kcal/mole. The two data points at 1000°C fall on either side of the line. The spread is no greater than that reported by Holden, et al.

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* Holden, R. B., Speiser, R., and Johnston, H. L., J. Am. Chem. Soc., 70, 3897, (1948)

2-) Zr_2Be_{17}

The first beryllide studied was Zr_2Be_{17}. A sample was suspended in the furnace from the analytical balance by means of a tantalum wire. The sample was heated to approximately 1200 °C, but, before any measurements could be made, the sample came into contact with the thermocouple, which fused to the sample destroying the thermocouple. The experiment was terminated and the sample removed. It was observed, as shown in Figure II, that the tantalum wire had also fused to the sample.

Following this experience with Zr_2Be_{17} tungsten wire was used to suspend samples. No difficulties have been encountered with the tungsten wire. Another specimen of Zr_2Be_{17} is available and the evaporation rate of this material will be determined at a later date.

3-) $ZrBe_{13}$

The evaporation rates for $ZrBe_{13}$ were measured over the temperature range 965 to 1165 °C. The weight loss as a function of time was found to be linear at all temperatures. Under the assumption that the evaporating species was monatomic beryllium, the vapor pressures were calculated from measured evaporation rates by means of the Langmuir equation. The evaporation rates and vapor pressures are listed below:

Temp. (°C)	Evaporation rate $(gm/cm^2/sec)$	Vapor pressure (atmospheres)
965	4.78×10^{-8}	1.263×10^{-8}
1000	1.39×10^{-7}	3.72×10^{-8}
1090	1.127×10^{-6}	2.795×10^{-7}
1165	4.98×10^{-6}	1.42×10^{-6}

It will be noted that the evaporation rate of $ZrBe_{13}$ is about a factor of four lower than that of beryllium metal, but still appreciable at the temperatures of measurement. For example, the rate of weight loss for $ZrBe_{13}$ at 1000 °C would be 12 milligrams per cm^2 per day.

X-ray diffraction patterns of the surface of the specimen were obtained before and after the evaporation experiments. The surface prior to evaporation was predominantly $ZrBe_{13}$ with some traces of Zr_2Be_{17}. After the experiments the surface was predominantly $ZrBe_2$.

Figure II.   Photograph of Tantalum Wire Fused to Zr_2Be_{17} Specimen

This suggests that the evaporation reaction is:

$$ZrBe_{13} \rightarrow ZrBe_2 + 11\ Be(g)$$

A chemical analysis of the deposit on the tantalum heat-shield which surrounded the specimen during the run was made. The results, while qualitative, indicate that the deposit is primarily beryllium with some zirconium. X-ray diffraction analysis of the heat-shield showed the presence of tantalum beryllides, predominantly $TaBe_3$ with some $TaBe_2$. This supports the hypothesis that the evaporating species is beryllium, although the fact that the chemical analysis showed the presence of some zirconium indicates that the evaporation reaction may be complex. In Knudsen effusion experiments with $ZrBe_{13}$ carried out by the Brush Beryllium Company* the surface is reported to be predominantly Zr_2Be_{17} and $ZrBe_5$ following evaporation. This indicates that in addition to the reaction given above, other possible decomposition reactions are:

$$2ZrBe_{13} \rightarrow Zr_2Be_{17} + 9Be(g)$$

$$ZrBe_{13} \rightarrow ZrBe_5 + 8Be(g)$$
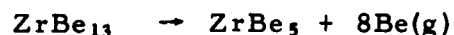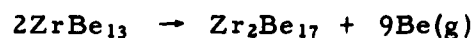
with the possible decomposition of the products of these reactions to $ZrBe_2$. If there were an intermediate step in the decomposition of $ZrBe_{13}$, it would be expected that a change in evaporation rate would be observed when the surface had been converted to the intermediate phase. Such a change was not observed in this investigation.

In Figure III the logarithm of the pressure (the pressures are those listed above which are computed assuming that the evaporating species is monatomic beryllium) is plotted against reciprocal temperature for $ZrBe_{13}$. In addition to the data determined in this investigation, three points determined by the Brush Beryllium Company* are shown in the figure. That two of the Brush data points fit in very well with the data from this investigation is obvious. The third Brush data point, at the highest temperature (1455°C) does not fall on or near the straight line. There is no reasonable explanation for this apparent inconsistency (see Discussion).

The equation for the straight line in Figure III is:

$$\log_{10} P \text{ (atmospheres)} = \frac{-18,590}{T} + 7.13$$

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* "Investigation of Intermetallic Compounds for Very High Temperature Applications," Brush Beryllium Company, Cleveland, Ohio, WADD-TR-60-889, Part II, July, 1962
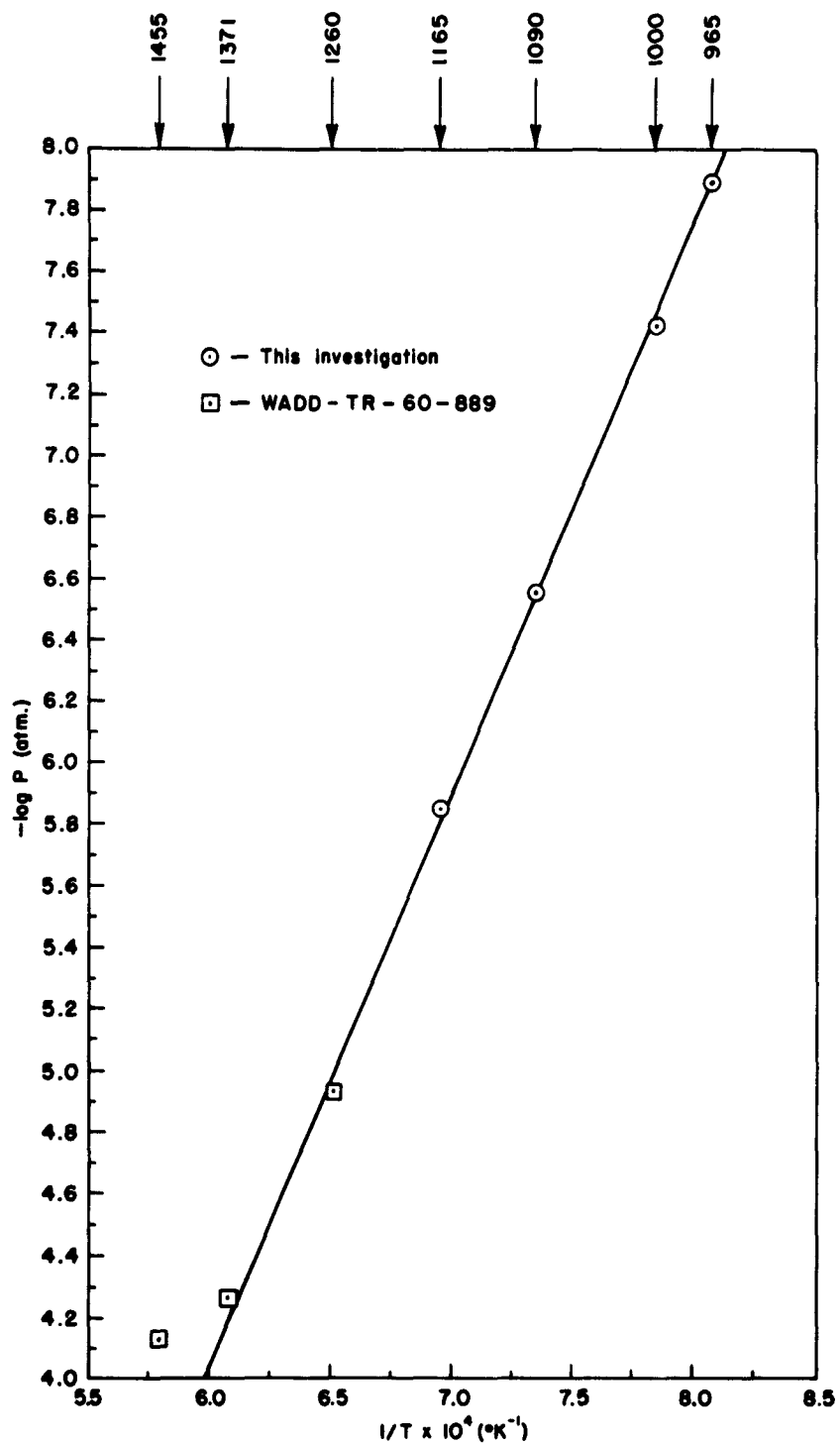
* Ibid.

Figure III. Van't Hoff Plot of Log P vs I/T for $ZrBe_{13}$

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The standard enthalpy of the evaporation reaction over the temperature range from 965 to 1370°C, ΔH_T^0, as computed from the slope of the line is 85.0 kilocalories per gram atom of beryllium. As indicated above it is not yet possible to specify precisely what the evaporation reaction is. The value of ΔH_T^0 given in the Brush Beryllium Company report is 38.2 kilocalories. Quite obviously, if the three data points obtained by Brush are considered by themselves, a line with a completely different slope would be drawn. Such a line gives a much lower value of ΔH_T^0 than that determined in this investigation.

4-) NbBe$_{12}$

The evaporation rates of NbBe$_{12}$ were measured over the temperature range from 950 to 1077°C. The first experiment was carried out at 950°C and for subsequent experiments the temperature was increased in 25°C intervals. The weight loss was observed to be a linear function of the time for temperatures up to and including 1025°C. A typical weight loss vs. time curve is shown in Figure IV where the data at 1025°C are plotted. At 1050°C a different phenomenon was observed as is shown in Figure V. A change in evaporation rate took place after about 40 minutes at temperature. The experiment was repeated and the same phenomenon was observed. Since the phenomenon is reproducible it must, at this time at least, be considered to be real. A change in evaporation rate could be caused by a change in the mechanism of the reaction. X-ray diffraction analysis of the surface of the specimen (originally pure NbBe$_{12}$) after evaporation indicated the presence of primarily NbBe$_3$ with small amounts of NbBe$_{12}$, Nb$_2$Be$_{17}$, Nb$_2$Be$_{19}$, and a significant amount of an unidentified phase. Obviously, as in the case of ZrBe$_{13}$, the evaporation reaction is complex. It could be that NbBe$_{12}$ decomposes to either Nb$_2$Be$_{17}$ or Nb$_2$Be$_{19}$ or to the unidentified phase which in turn decompose to NbBe$_3$. This could account for a change in evaporation rate when the surface becomes depleted in NbBe$_{12}$. Another possibility is that the rate of evaporation becomes diffusion controlled when the surface is depleted of beryllium. The true explanation of the change in evaporation rate cannot be given at this time. A discussion of a possible explanation is presented following the report of results obtained for Nb$_2$Be$_{17}$.

The tantalum heat shield surrounding the specimen was analyzed by X-ray diffraction after the evaporation experiments and the presence of TaBe$_3$ with minor amounts of TaBe$_2$ was observed. This supports the assumption that the evaporating species was monatomic beryllium.
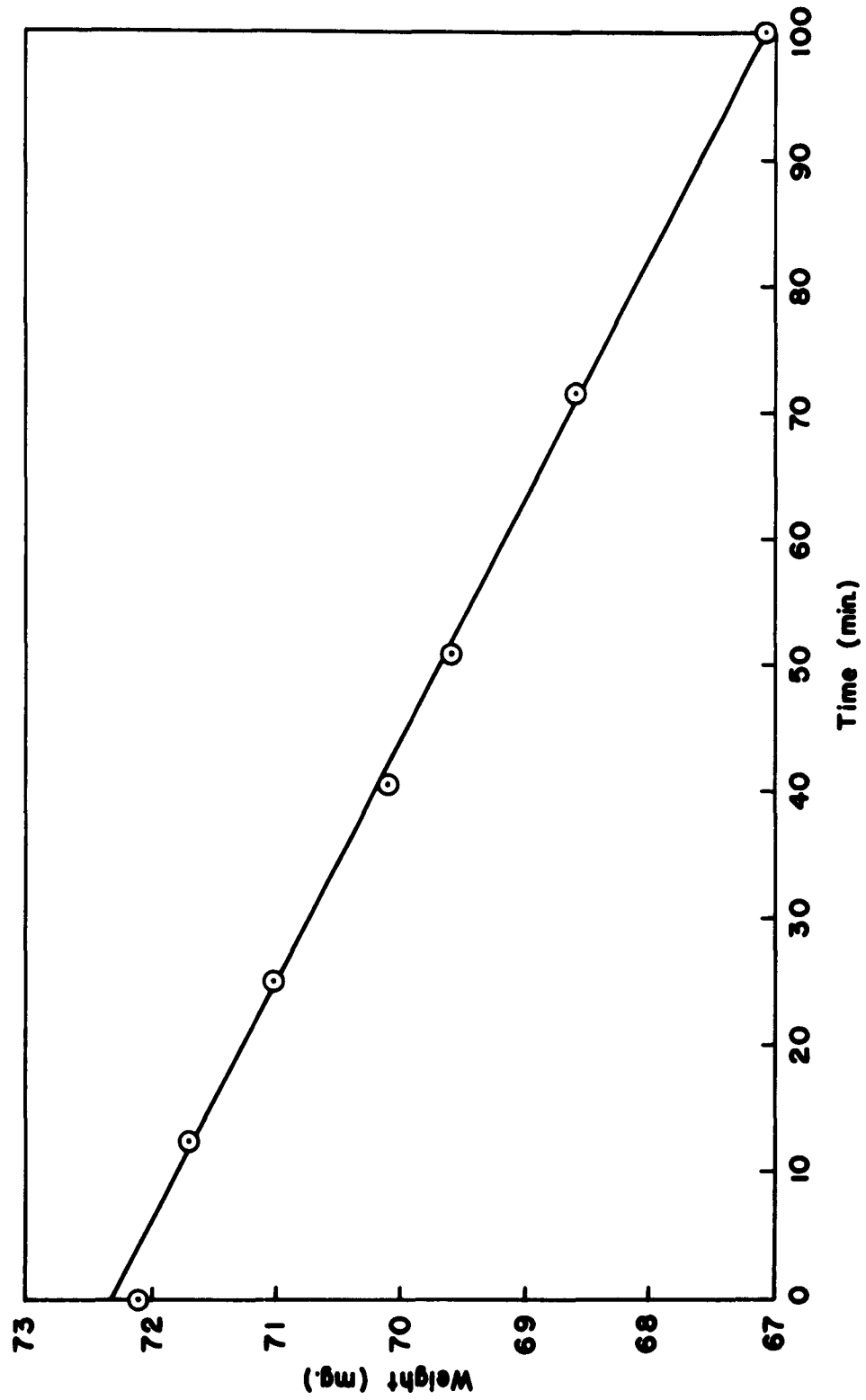
Figure IV. Weight Loss vs Time for NbBe₁₂ at 1025°C

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Weight (mg.)

6.8 6.7 6.6 6.5 6.4 6.3 6.2

(1)

(2)

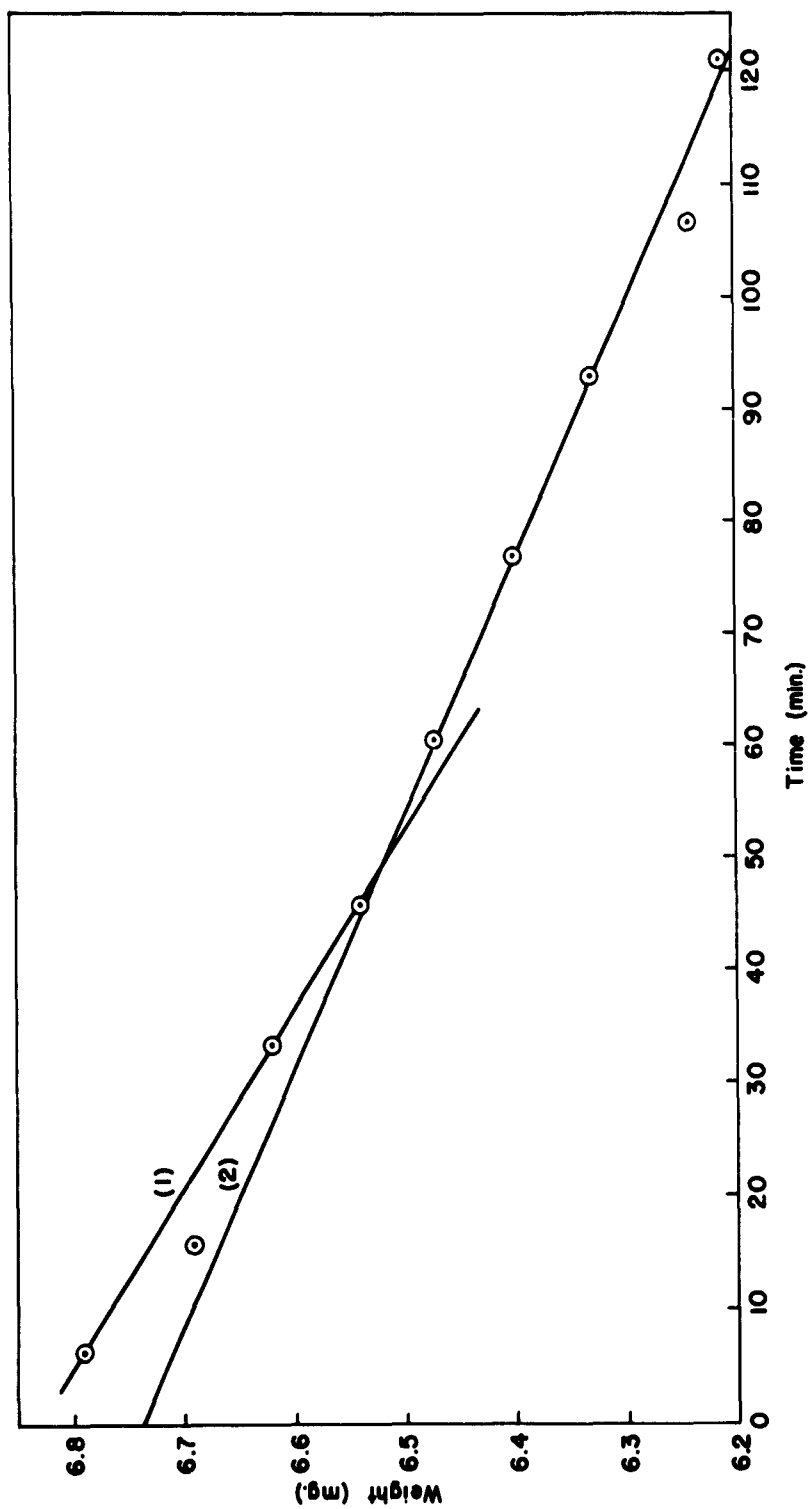0 10 20 30 40 50 60 70 80 90 100 110 120

Time (min.)

Figure V. Weight Loss vs Time for NbBe$_{12}$ at 1050°C

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With this assumption evaporation rates were converted to vapor pressures using the Langmuir equation with the results given below:

Temp. (°C)	Evaporation rate (gm/cm²/sec)	Vapor pressure (atmospheres)
950	8.89×10^{-8}	2.335×10^{-8}
975	1.112×10^{-7}	2.95×10^{-8}
1000	1.198×10^{-7}	3.21×10^{-8}
1025	1.352×10^{-7}	3.66×10^{-8}
1050	1.622×10^{-7} (fast)	4.43×10^{-8}
	1.138×10^{-7} (slow)	3.105×10^{-8}
1050 (repeated)	1.657×10^{-7} (fast)	4.53×10^{-8}
	1.049×10^{-7} (slow)	2.86×10^{-8}
1077	1.729×10^{-7}	4.77×10^{-8}

In Figure VI the logarithm of the pressure is plotted against reciprocal absolute temperature using the data for $NbBe_{12}$ given above. At 1050°C the points corresponding to the fast evaporation rate fall on the lower line while the points corresponding to the slow rate fall on the upper line. The equation for the lower line is:

$$\log_{10} P(\text{atmospheres}) = \frac{-4350}{T} - 4.07$$

The slope of this line gives ΔH_T^0 equal to 19.9 kcal per gram atom beryllium. The equation of the upper line is:

$$\log_{10} P(\text{atmospheres}) = \frac{-13,000}{T} + 2.31$$

and ΔH_T^0 is equal to 59.5 kcal/gram atom Be.

The data point in Figure VI at 1075°C might be considered to fall on either line drawn. The data is insufficient to determine whether or not this represents an intersection of the two lines and, hence, a triple point on the Nb-Be phase diagram. Data at this temperature will be redetermined and data at higher temperatures will be obtained to better define the behavior of the system in this temperature range.
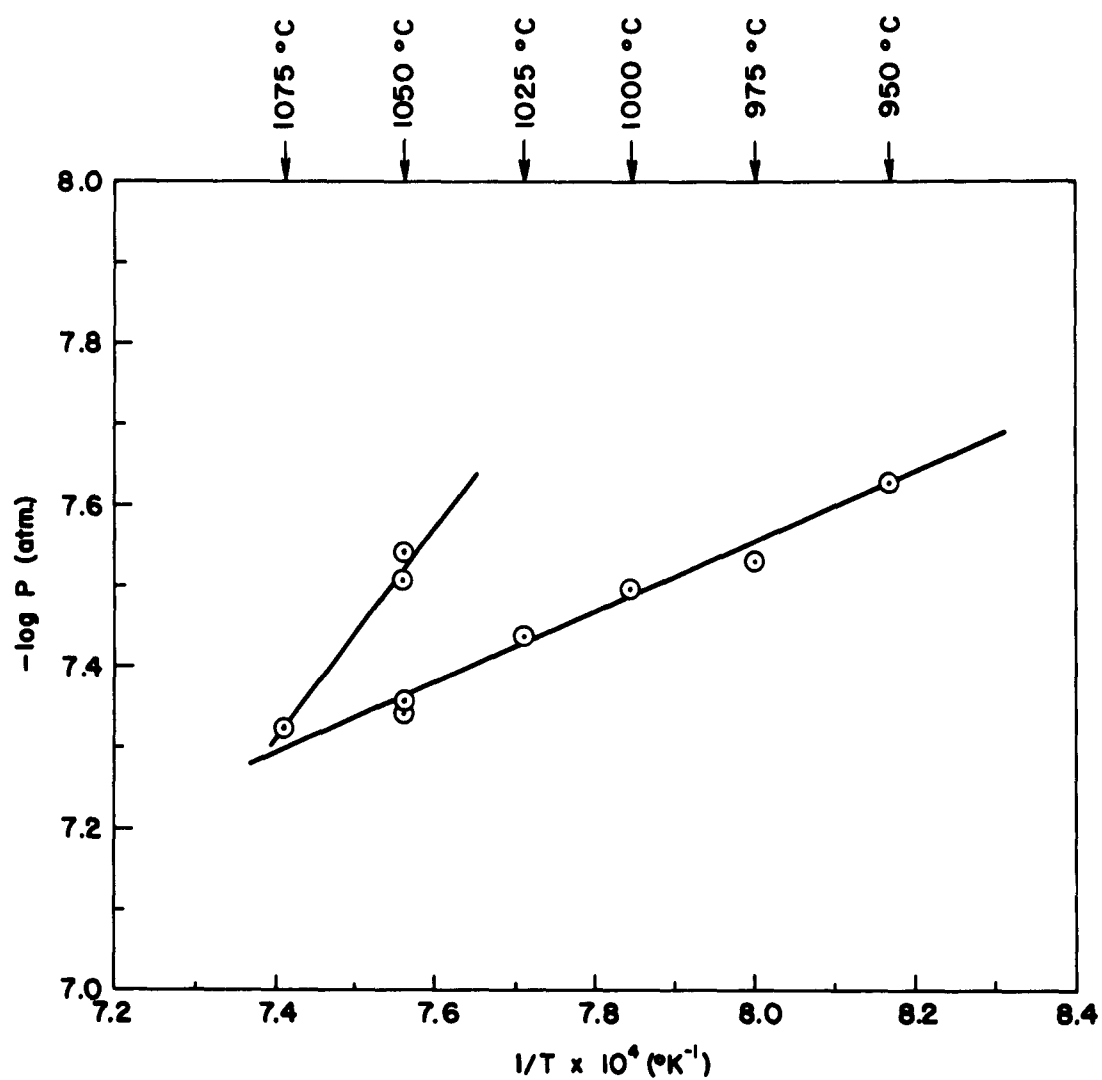
Figure VI. Van't Hoff Plot of Log P vs I/T for NbBe$_{12}$

5-) Nb_2Be_{17}

Evaporation rates of Nb_2Be_{17} were determined in the temperature range from 950 to 1050°C. As in the case of $NbBe_{12}$, a change in rate was observed. In this case the change occurred at 975°C. The fact that only one indication of this change has been observed so far throws some doubt on the reality of the observation; however, until additional data confirm or disprove the existence of the change, it will be considered to be real. Again it was assumed that monatomic beryllium was the evaporating species and vapor pressures were calculated from measured evaporation rates. The results are given below:

Temp. (°C)	Evaporation rate (gm/cm²/sec)	Vapor pressure (atmospheres)
950	6.255×10^{-8}	1.638×10^{-8}
975	1.462×10^{-7} (fast)	3.86×10^{-8}
	4.23×10^{-8} (slow)	1.123×10^{-8}
1000	6.87×10^{-8}	1.84×10^{-8}
1025	8.80×10^{-8}	2.38×10^{-8}
1050	1.513×10^{-7}	4.14×10^{-8}

In Figure VII a Van't Hoff plot of the above data is presented. The lower line corresponds to the data at 950°C and the fast evaporation rate at 975°C. The upper curve corresponds to the slow rate at 975°C and the data at the higher temperatures. The equation for the lower line is:

$$\log_{10} P(\text{atmospheres}) = \frac{-21,400}{T} + 9.70$$

and ΔH_T^0 calculated from the slope of this line is 98.0 kcal/gram atom Be. The equation of the upper line is:

$$\log_{10} P(\text{atmospheres}) = \frac{-12,200}{T} + 1.83$$

and ΔH_T^0 is 55.8 kcal/gram atom Be.

X-ray diffraction analyses of the specimen before evaporation indicated the presence of predominantly Nb_2Be_{17} with small amounts of $NbBe_{12}$. After evaporation the surface was predominantly $NbBe_3$ with significant amounts of the same unidentified phase observed after evaporation of $NbBe_{12}$ and with small amounts of Nb_2Be_{17}, Nb_2Be_{19}, and $NbBe_{12}$.

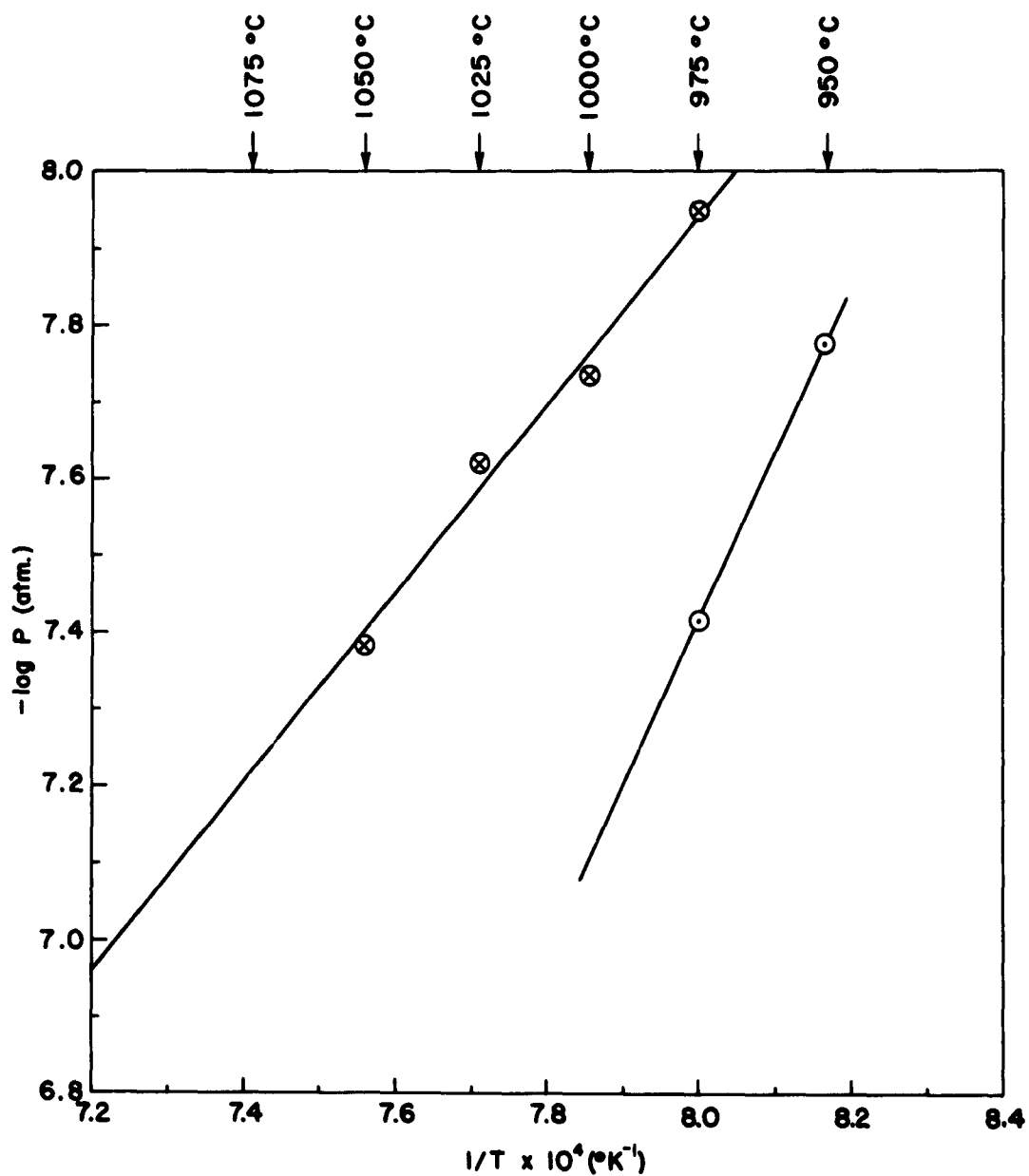Figure VII. Van't Hoff Plot of Log P vs I/T for Nb_2Be_{17}

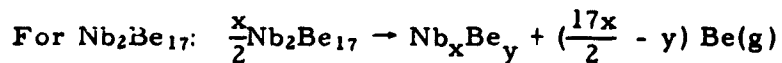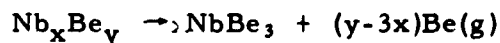DENVER RESEARCH INSTITUTE — UNIVERSITY OF DENVER

E.   Discussion of Results

The results obtained so far in this investigation suggests that $ZrBe_{13}$ decomposes to $ZrBe_2$. This is in contradiction to data obtained by the Brush Beryllium Company* which indicate that the decomposition products are Zr_2Be_{17} and $ZrBe_5$. It is quite conceivable that $ZrBe_{13}$ should decompose to these intermediates which in turn decompose to $ZrBe_2$. However, the Brush data were obtained at higher temperatures than those employed in this investigation and if Zr_2Be_{17} and $ZrBe_5$ are the stable species at the higher temperatures they should be the stable species at the lower temperatures. More data are needed to explain this apparent contradiction. Studies of the evaporation rates of Zr_2Be_{17} and the lower beryllium content beryllides of zirconium (which are planned for the immediate future in this program) should provide the necessary information.

The results obtained for $NbBe_{12}$ and Nb_2Be_{17}, while as yet inconclusive, permit an hypothesis of the decomposition characteristics of the niobium-beryllium intermetallic compounds. Assuming that there are, indeed, two reactions involved in the decomposition of $NbBe_{12}$, to the final product $NbBe_3$, a logical sequence would be:

$$2NbBe_{12} \rightarrow Nb_2Be_{17} + 7Be(g)$$

$$Nb_2Be_{17} \rightarrow 2NbBe_3 + 11Be(g)$$
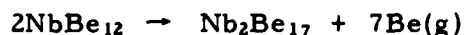
If this were the case, Nb_2Be_{17} would be expected to decompose to $NbBe_3$ in a single step. Although, as indicated above, the data are by no means conclusive, the evidence indicates that Nb_2Be_{17} decomposes in a two step process. There is no known intermetallic compound in the Nb-Be system with beryllium content between Nb_2Be_{17} and $NbBe_3$. However, as pointed out above, an unidentified phase was found to be present on the surface of both the $NbBe_{12}$ and Nb_2Be_{17} specimen following evaporation. Coupling this with the facts that the slopes of the upper lines in both Figures VI and VII are almost the same and that an error in temperature of about 15 °C could have displaced one line with respect to the other, that is, that the two lines could represent the same reaction, the following decomposition reactions are suggested:

For $NbBe_{12}$: $xNbBe_{12} \rightarrow Nb_xBe_y + (12x-y)Be(g)$

$Nb_xBe_y \rightarrow NbBe_3 + (y-3x)Be(g)$

For Nb_2Be_{17}: $\dfrac{x}{2}Nb_2Be_{17} \rightarrow Nb_xBe_y + (\dfrac{17x}{2} - y) Be(g)$

$Nb_xBe_y \rightarrow xNbBe_3 + (y-3x) Be(g)$

* Ibid.

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where Nb_xBe_y represents the unidentified phase. It is noted that the second reactions in both decomposition mechanisms is the same and this is the reaction which presumably corresponds to the upper lines in Figures VI and VII.

In order to determine whether or not the above reactions actually do take place in the decomposition of the niobium beryllides, an attempt will be made to prepare the Nb_xBe_y phase in pure form and identify it. In addition evaporation rates for these compounds will be determined at both higher and lower temperatures and the accuracy of the data obtained so far will be checked by repeating the experiments with different specimens.

IV.   THERMIONIC EMISSION STUDIES

The original intention in this program (and one that has not been abandoned completely) was to use the Schottky plot method as utilized by George A. Haas of the Naval Research Laboratory in his work on uranium carbide* for the determination of the thermionic emission parameters, work function and Richardson's A value, for intermetallic compounds, beginning with the beryllides. In this technique a refractory metal wire is coated with the material being studied and the wire is used as the cathode in a diode with cylindrical geometry. The emitter is heated simply by utilizing the resistance heating of the wire. High fields between emitter and collector are possible with relatively low potential differences because of the small diameter of the wire. An essential requirement for using this technique is, of course, that uniform, adherent coatings of the material being studied can be deposited on refractory metal wires. Haas** used a cataphoretic (electrophoretic) technique for depositing UC on tungsten wires. J. B. Baker and G. B. Gaines at the Battelle Memorial Institute† were successful in depositing rare-earth metal oxides on refractory metal wires by this means. It was felt that the cataphoretic technique was the one best suited for preparing coatings of beryllides for emission studies in this program.

Although no full-blown experimental program was instituted, a number of experiments were carried out in cataphoretic coating. It was found possible to prepare oxide coatings following the method of Baker and Gaines, but this method (and what modifications were made in the application of the method) did not produce coatings of beryllides. There are a great many parameters which affect cataphoretic deposition. One of the most crucial is particle size within the coating suspension and this, in our case, could not be closely controlled. It was felt that a thorough study of this technique would require more time and effort than was considered appropriate at that time. It was decided that, while some consideration would be given to cataphoretic and other coating methods for

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*   Haas, G. A., and Jensen, J. T., Jr., J. Appl. Phys., 31, 1231, (1960), and Haas, G. A., and Harris, F. H., Rev. Sci. Instr., 30, 623, (1959).

**   Ibid.

†   Baker, J. B., and Gaines, G. B., "Final Report: Investigation of Rare-Earth Oxide Cathodes," Battelle Memorial Institute, Columbus, Ohio, AFCRL 183, March 1961.

the preparation of emitter specimens for Schottky plot determinations, another method for the determination of emission constants which would utilize more massive specimens of the beryllides should be adopted. The technique used by J. M. Lafferty of the General Electric Research Laboratory for studying the alkaline earth and rare earth borides* seemed the most appropriate because it is relatively simple, and the equipment could be modified for the Haas-Schottky plot technique at a later time if desired.

Although no emission measurements have as yet been made in this program, considerable time and effort have gone into the design and construction of equipment for such measurements by means of the Lafferty technique and into the fabrication of emitter specimens for use in this equipment. The progress made, as well as the set-backs, encountered in this phase of the program are described below.

A.   Experimental Apparatus

The apparatus to be used for the determination of emission constants consists of a water-cooled glass diode which contains the emitter and collector elements, a high vacuum system for the evacuation of this diode, and the necessary power supplies and instrumentation.

1-) The Diode

A preliminary model of the diode was designed and constructed. This diode (Figure VIII) consists of a glass envelope, the major portion of which is surrounded by a glass cooling jacket. A circular sighting port, which can be covered when not in use by a magnetic pyrex coated pellet, is located in the end of the diode to permit measurement of the emitter temperature by means of an optical pyrometer.

The emitter element, a cylindrical sample of the material to be studied, is located along the axis of the diode. It is supported on molybdenum forks which are clamped to radially placed tungsten rods sealed into side arms in the diode wall. The emitter is surrounded by a coil which serves as both the heater and collector. The coil is divided into three separate sections, the length of the center coil being equal to the sum of the lengths of the end coils. The coils are independently attached to radial tungsten leads which extend through the wall of the diode. The three coils are kept at a positive potential difference of about 400 volts

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* Lafferty, J. M., J. Appl. Phys., 22, 299, (1951).

Figure VIII.   Photograph of First Preliminary Model of Diode for Measurement of Thermionic Emission Constants

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with respect to the emitter. The end coils serve as guard rings, collecting the emission current from the ends of the sample. The center coil is used to collect emission current from the constant temperature zone of the emitter.

The coils were fabricated by wrapping 20-mil tungsten wire on a 5/16" National Fine Cap Screw. The wire was heated with a benzene torch during fabrication and later annealed. The electrical circuit used for heating and detection of emission current is shown in Figure IX.

This first preliminary diode has proved to be very fragile. The tungsten to glass seals, which are very difficult to make, vacuum tight in the first place, are subject to cracking when even the slightest stress is applied in the alignment of coils and specimen within the diode. The fragility of the first diode led to a redesign which provides for much stronger metal to glass seals and more overall sturdiness.

The modifications incorporated in the second diode are: 1) simplification of the glass envelope design, so that fabrication of a leak free diode can be accomplished with less difficulty, 2) provision of additional support for the tungsten leads, so that the welded tungsten to Kovar seals will not be highly stressed, and 3) more accessibility of the coils and emission sample for alignment. The modified design is shown in Figure X. In this diode, which is in the process of being fabricated, the element geometry remains unchanged. However, the tungsten leads are sealed into a flat glass single wall, rather than a curved double wall. Spacers act as heat shields to protect the uncooled end of the diode where electrical connections are made. Since the spacers are not connected to the glass envelope it will be possible to remove the entire assembly for alignment and replacement of emitter specimens by simply cutting the diode near the end into which the leads are sealed and sliding the assembly from the tube.

The sighting port and cooling jacket have been retained essentially as in the first preliminary design. The vacuum connection has been relocated in the side of the diode.

2-) Vacuum System

The vacuum system to be used in these studies was procured from Varian Associates, Palo Alto, California. In order to obtain the cleanest system possible, an 8 liter per second Vac Ion pump was chosen for continuous high vacuum pumping. It is to be used in conjunction with a Vac
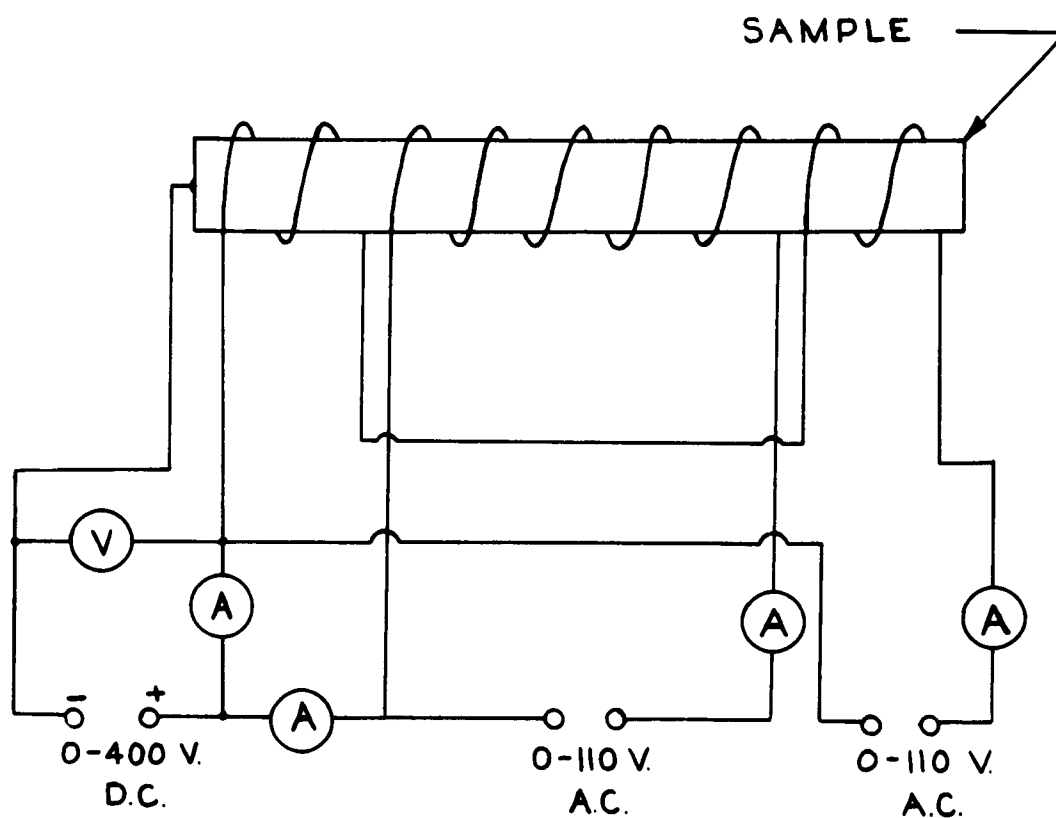
SAMPLE

0-400 V.
D.C.

0-110 V.
A.C.

0-110 V.
A.C.

Figure IX. Electrical Circuit for Heating Emitter and Measuring
Emission Current
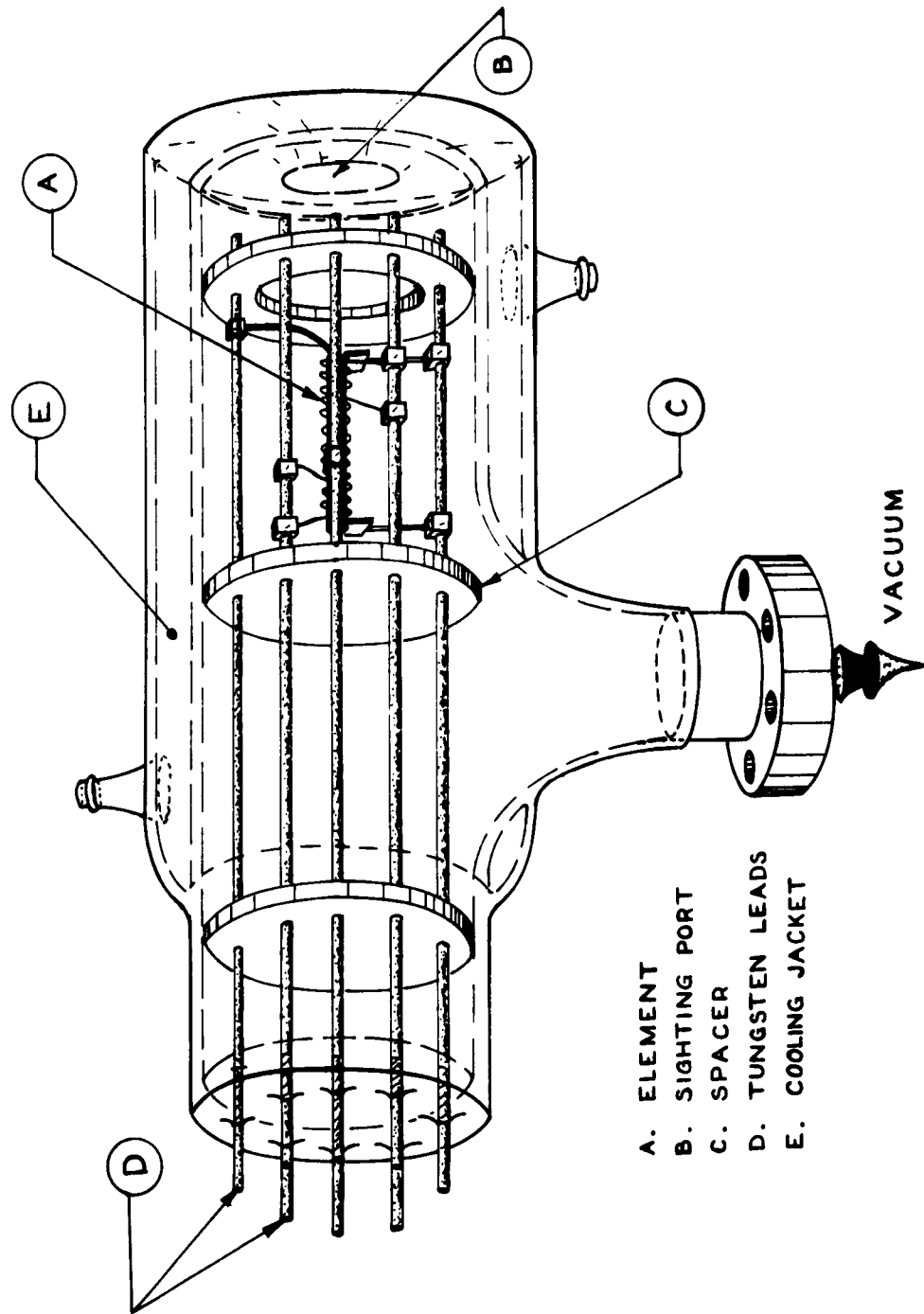
Figure X. Sketch of the Second Diode for Measurement of Thermionic Emission Constants

A. ELEMENT
B. SIGHTING PORT
C. SPACER
D. TUNGSTEN LEADS
E. COOLING JACKET

VACUUM

Sorb roughing pump. This system was chosen because of its cleanliness, high ultimate vacuum, and because pumping could be continued during operation of the diode. During tests using the first preliminary model of the diode this system has proven to be quite satisfactory and no modification of the pumping system is planned. A sketch of the vacuum system is shown in Figure XI.

All items of major equipment used in this program, such as the high vacuum system described above, have been, and will be, purchased by the University of Denver and not out of contract funds.

B.   Preparation of Emitter Specimens

As indicated above the emitter specimens to be used for measurement of emission constants by the technique developed by Lafferty are cylindrical in shape. The dimensions of these specimens should be about 0.2 inches in diameter and 1-1/4 inches long. Ideally these cylinders should have a hole drilled in one end to a depth of about 1/2 inch for measurement of temperature by optical means. Considerable effort has been expended in attempts to prepare specimens of $ZrBe_{13}$ of these dimensions. A number of fabrication techniques have been utilized with the results described below.

1-) Isostatic Pressing

In order to obtain a sample of uniform density throughout, isostatic pressing of reacted $ZrBe_{13}$ powder was attempted. Molds used for pressing were four inch long sections of rubber tubing, 1/8" ID and 3/8" O.D. The tubing was closed at one end with a vacuum seal-off clamp. A funnel was used to fill each of three sections of tubing with the powder. The molds were then tamped on a hard surface to settle the powder. This procedure was repeated until each tube appeared to be full. Another vacuum seal-off clamp was then used to close the other end of each piece of tubing.

The pressing operation was performed at Coor's Porcelain Company in Golden, Colorado. The three samples were subjected to isostatic pressures of 3000, 4000 and 5000 psi, respectively. Upon opening the rubber tubing, it was found that very little compacting had taken place at any of the three pressures used. From the appearance of the resulting powder, it was concluded that much higher pressures and more rigid dies would be needed if a cylindrical compact was to be obtained. An isostatic pressure apparatus capable of producing pressures much in excess of 5000 psi was not available. Hence, this technique was pursued no further.
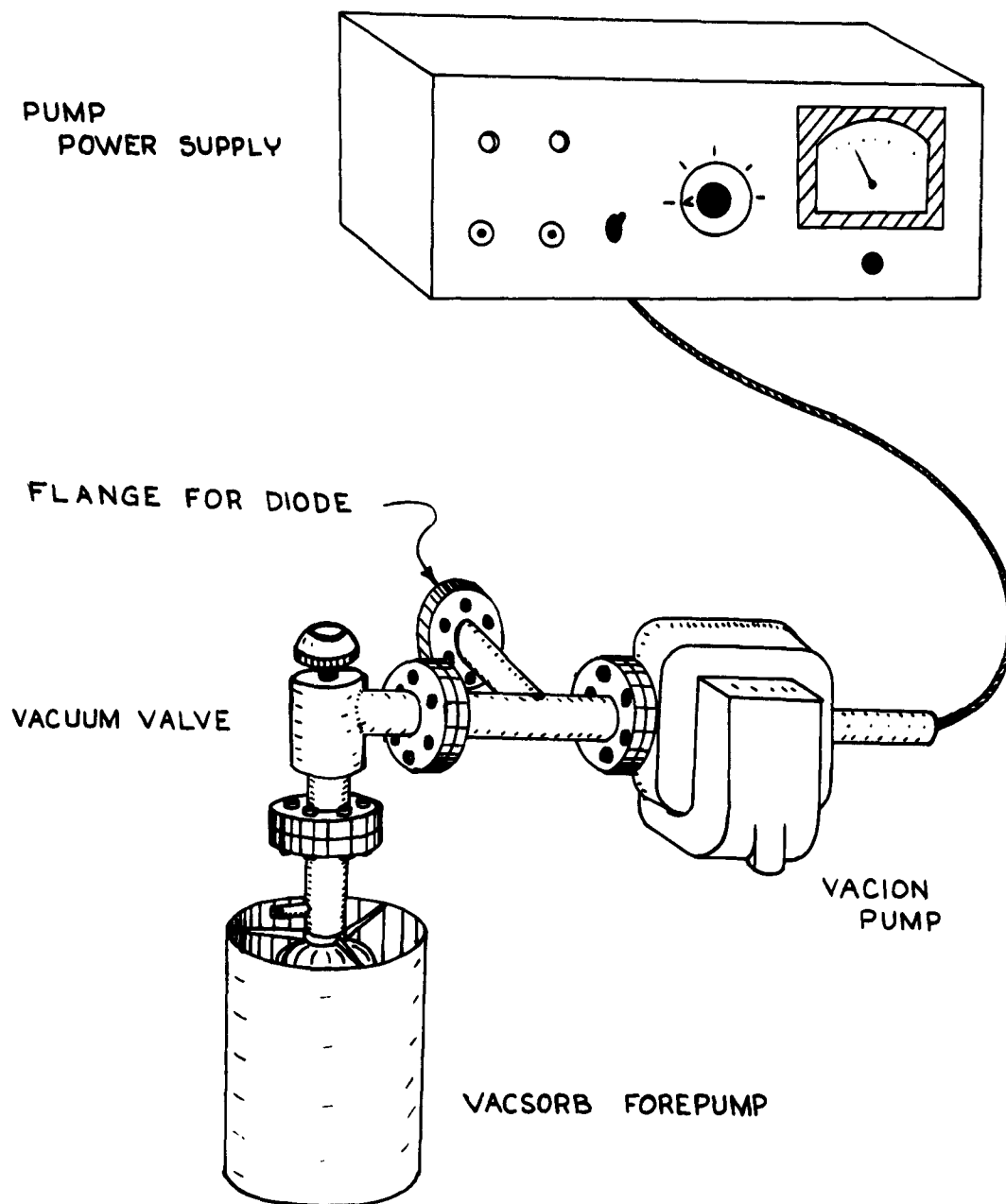
PUMP
POWER SUPPLY

FLANGE FOR DIODE

VACUUM VALVE

VACION
PUMP

VACSORB FOREPUMP

Figure XI. Sketch of the High Vacuum Pumping System to be Used with Emission Constants Measuring Diode

2-) Extrusion

The extrusion of a $ZrBe_{13}$ rod was attempted with two extrusion mixes. The first mix had the following composition:

$ZrBe_{13}$ powder	-	80 wt%
water	-	11 wt%
glycerin	-	5 wt%
corn starch	-	4 wt%

It was found that this mixture tended to compact in the die: the liquid components extruded preferentially leaving a relatively dry mixture in the die. The result was an excessively wet rod which failed to maintain its shape satisfactorily. The second type of mix used contained only Nopco GS-15 emulsion in addition to $ZrBe_{13}$ powder. The composition was varied over the range 0 to 25 weight percent Nopco GS-15; and it was found, for all compositions, that the preferential extrusion of liquids was even more serious than that obtained with the corn starch mix.

Two die configurations differing in angle of convergence and plunger design were employed, but little difference in effectiveness was noted.

3-) Slip Casting

Slip casting was attempted using a slip composed of $ZrBe_{13}$ powder suspended in a 3% aqueous solution of polyvinyl alcohol. A plaster of Paris mold with no release agent was employed. After casting, the greenware adhered tightly to the mold surface. In addition, the slip failed to fill the mold, and the structure of the casting where the mold had been filled was extremely porous.

4-) Cold Pressing

Of the processes attempted, cold pressing appears to offer the greatest possibility of producing satisfactory specimens. After some investigation of the effects of compacting sequences and pressures it was possible to produce rods up to 1-1/2 inches in length with the required diameter. However, these rods have not been of uniform density and have tended to fracture during vacuum bake out.

For uni-axial pressing from one end it was found that compacting pressures exceeding about 9000 psi resulted in cracking and excessive

wall friction when the specimen was pressed from the die. However, pressures on the order of 8000 psi could be effectively employed to produce rods up to 1-1/2 inches in length.

In an attempt to reduce the variation in density of the rods, uni-axial pressing from both ends at pressures ranging from 4000 to 8000 psi was attempted. In all cases, the wall friction was too great to permit smooth removal of the rod and fracture resulted.

A third method of compacting was employed in which the specimen was pressed uni-axially from one end and then removed from the die by pressing from the opposite end. Owing to the wall friction, this procedure resulted in compacting of both ends of the rod. It was found that with an initial compacting pressure greater than 4000 psi, pressures greatly in excess of 9000 psi were required for removal of a 1-1/4 inch specimen. However, when the initial compacting pressure was between 3000 and 4000 psi removal pressures on the order of 8000 psi were required. The resulting specimens were crack free and considerably more uniform than those obtained when the specimen was removed in the same direction as it was pressed.

Best results were obtained by this technique when the powder mixture was pre-compacted at a pressure of approximately 8000 psi. The resulting compact was fragmented by means of a spatula and its ends used in the final pressing process. A photograph of a cold pressed specimen of the required dimensions is shown at the bottom of Figure XII.

The binder used for all specimens prepared by cold pressing was Carbowax 1500, approximately 10% by volume. Carbowax and glycerin were both used as mold lubricants: glycerin proved to be generally more effective.

5-) Sintering

Sintering of the cold pressed compacts has been attempted, under dry hydrogen, at a temperature of 2800°F. During the preliminary sintering operations in an open Al_2O_3 boat it became evident that physical constraint of the specimen would be needed to prevent warpage of the specimen. Also a reaction occurred resulting in a "growth" along one side of the specimen. The warpage and "growth" can be seen in the photograph of a sintered specimen at the top of Figure XII.

Figure XII. Photograph of Cold Pressed $ZrBe_{13}$ Specimens. Bottom: Unsintered. Top: Sintered in Open Al_2O_3 Boat.

At the Brush Beryllium Company* cold pressed beryllide specimens have been successfully sintered in BeO containers under an atmosphere of dry helium. This technique will be used in future sintering operations using a hollow BeO cylinder to hold the green specimen in order to prevent warpage. It is expected that, due to volatilization of Be from the beryllides, the outermost surface of the sintered samples will have to be removed by grinding. A grinder supplied with a speed reducer has been procured for this purpose.

C.   Conclusions

With the lessons learned in the fabrication of the first preliminary diode and the resulting improvements which have been incorporated in the second diode design, it is felt that the apparatus for measuring emission constants is well on the way towards providing definitive data. One difficulty that remains is the preparation of satisfactory emitter specimens. From experience gained so far, it appears that of the fabrication methods available to us on this program, cold pressing followed by sintering offers the best chance of success. In a sense the work we have done on fabrication techniques for the beryllides is a duplication of work carried out by the Brush Beryllium Company**. Workers at Brush have been able to fabricate various shaped specimens of beryllides by a number of techniques. The best technique, however, appears to be hot pressing and subsequent grinding to final size and shape. Unfortunately, there is no equipment available at the University of Denver for the hot pressing and precision grinding of beryllides. Through correspondence, the Brush Beryllium Company has informed us that they can fabricate cylindrical specimens in the size required in this program of some of the beryllides. These include the high beryllium content beryllides of zirconium, niobium, and tantalum. Since we are interested in the lower beryllium content beryllides of these and other metals as well as the high beryllium content compounds, we will proceed with cold pressing sintering experiments aimed primarily at the successful fabrication of low beryllium content beryllides.

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*   "Investigation of the Effects of Processing Variables and Fabrication Techniques Upon the Properties of Intermetallic Compounds," Brush Beryllium Company, Cleveland, Ohio, ASD-TDR-62-476, June 1962.

**   Ibid.

V.   CESIUM COMPATIBILITY STUDIES

Late in the first year contract period attention was focused upon the compatibility of intermetallic compounds with cesium vapor. The apparatus for carrying out these studies was designed and is shown in Figure XIII. It consists of a constant temperature furnace wherein several samples can be loaded, a cesium reservoir surrounded by a heater, and a break mechanism for breaking the cesium ampules. A stainless steel screen will be used to strain the cesium so that no glass enters the reservoir. The entire system will be evacuated to a vacuum of about 1 micron before introducing the liquid cesium.

The apparatus is presently under construction and should be finished shortly. Immediately upon completion, the compatibility with cesium of the available intermetallic beryllides will be studied at temperatures up to 1000°C for periods of 24 to 48 hours.
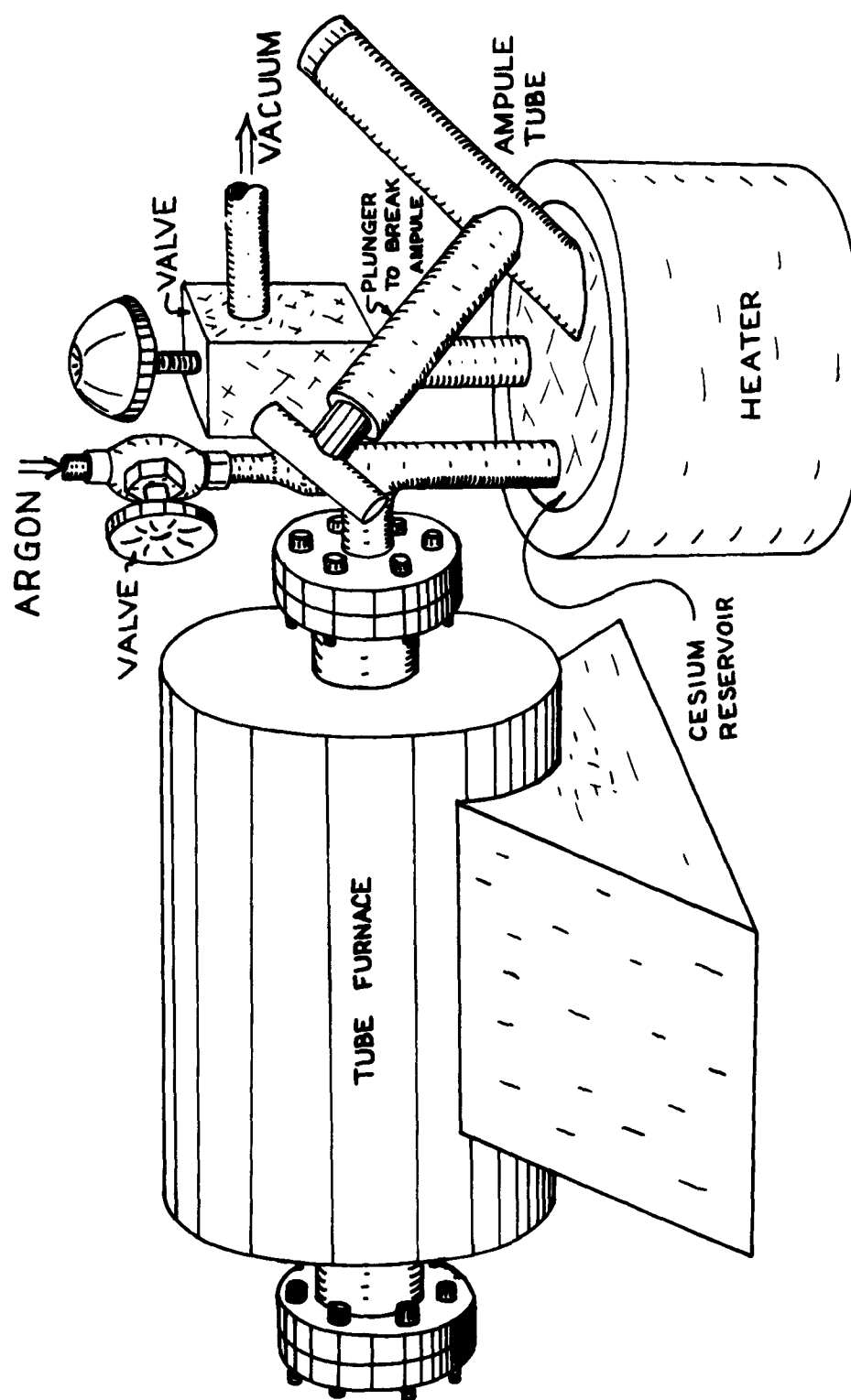
Figure XIII. Sketch of Apparatus for Determining Compatability of Intermetallic Compounds with Cesium

APPENDIX A

Some Intermetallic Compounds Melting Above 1200°C

Compound	Melting Point (°C)	Crystal Structure	Type	Compound	Melting Point (°C)	Crystal Structure	Type
Al_4Ce	1245	$D1_3$		Be_3Ta		Rhomb.	
Al_2Ce	1460	C15		Be_2Ta		C15	$MgCu_2$
AlCo	1645	B2	CsCl	Be_2Ta_3		Tetra	U_3Si_2
AlNi	1638	B2		$Be_{12}Ti$		$D2_b$	$ThMn_{12}$
$AlNi_3$	1390*	$L1_2$		$Be_{17}Ti_2$		Rhomb.	Nb_2Be_{17}
Al_3V	1360	DO_{22}		Be_2Ti		C15	$MgCu_2$
Al_2Zr	1645			Be_3Ti		$R\bar{3}m$	$NbBe_3$
Al_2Zr_3	1480			$Be_{13}V$	3100*	hex	VBe_{12}
Al_3Zr_4	1530			Be_2V		C15	$MgCu_2$
$AsMn_7$	1400			$Be_{20}W$		O_h^7 or T_h^4	
As_3Pt_2	1460*			$Be_{16}Zr$	1600		
Au_2Ti	1480			$Be_{13}Zr$	1900	$D2_3$	
Au_3Zr	1560			Be_9Zr	1750		
BeCo	1505	B2		$Be_{17}Zr_2$	1950*	Rhomb.	Nb_2Be_{17}
Be_2Cr	1840	C14		Be_6Zr	1530*		
$Be_{12}Cr$		$D2_b$	$ThMn_{12}$	Be_2Zr	1200*	C32	AlB_2
Be_2Fe	1480	C14		Ce_2Si	1460	Ortho.	
$Be_{20}Mo$		O_h^7 or T_h^4		$CeSi_2$	1440*	bct ($D2_b$)	$ThSi_2$
Be_2Mo	3340*	C14		CeSn	1400		
$Be_{12}Mo$		$D2_b$	$ThMn_{12}$	Co_4Zr	>1500		
$Be_{12}Nb$	1690	$D2_b$	$ThMn_{12}$	Cr_2Nb	>1660		
$Be_{19}Nb_2$	1700	hex		Cr_3Si	1730*	A15	
$Be_{17}Nb_2$		Rhomb.		Cr_2Si	1610*		
Be_3Nb		Rhomb($R\bar{3}m$)		CrSi	1560	B20	
Be_2Nb		C15	$MgCu_2$	$CrSi_2$	1550*	C40	
Be_2Nb_3			V_3Si_2	Cr_3Ta_2	1940	hex	
BeNi	1472	B2		Cr_2Ta		$D4_h$	
$Be_{20}Re$		O_h^7 or T_h^4		Cr_2Zr	1860	f. c. c.	
$Be_{12}Ta$	1980	$D2_b$	$ThMn_{12}$	Fe_3Mo_2 or Fe_7Mo_6	1480	hex	
$Be_{17}Ta_2$	1990	Rhomb.	Nb_2Be_{17}	FeMo	1540		

APPENDIX A (Cont.)

Compound	Melting Point (°C)	Crystal Structure	Type	Compound	Melting Point (°C)	Crystal Structure	Type
Fe_5Nb_3	1650			Si_2Ta	2200*	C40	
FeSi	1410	B20		Si_3Ta_5	trans 1700* 2500*	$D8_1$	
Fe_2Ta	>1900	C14		$SiTa_4$	2510	DO_{19}	
Fe_2Ti	1500*	hex		Si_2Ti	1540		
FeTi	1320	B2	CsCl	SiTi	1760	C_{2v}^1 or D_{2h}^1	
Fe_3Zr	1530	Cubic		Si_3Ti_5	trans 860* 2120	$D8_8$	
Fe_2Zr	1630*	f. c. c.		Si_2V	1650	hex	
Ge_2Mo_3	1700*			Si_2W	2100*	D_{4h}^{17}	
Ge_2Nb	1500*	C40		Si_2W_3	2320		
$GeNb_3$	1700*	A15		Si_2Zr	1520	D_{2h}^{17}	
Ge_3Ti_5	>1400	$D8_8$		Si_6Zr_5	2250		
Ge_2Zr	1520	C49		SiZr	2100	D_{2h}^{16}	
GeZr	2240	Complex		Si_4Zr_6	2250		
Ge_3Zr_5	2330	$D8_8$		Si_3Zr_4	2230		
$GeZr_3$	1585*	hex		Si_2Zr_3	2200	D_{4h}^5	
Mo_3Si	2100*	A15		$SiZr_2$	2110	C16	
Mo_5Si_3	2050	$D8_8$		$SiZr_4$	1630		
Mo_3Si_2	2190*	D_{4h}^{18}		Sn_3Zr_2	1980*		
$MoSi_2$	2000*	$C11_6$		$SnZr_2$	1950	hex	
Mo_2Zr	1880	Cubic		V_2Zr	1750	C14	$MgZn_2$
$NbNi_3$	1400	hex		W_2Zr	2170	Cubic	
Nb_4Si	1950		Ta_4Si				
Nb_5Si_3	2400*	O_{2d}^{11}					
$NbSi_2$	2000	C40					
Ni_3Ta	1550	hex					

* Approximate Melting Point

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INVESTIGATION OF THE CHARACTERISTICS OF INTER-METALLIC COMPOUNDS AS THERMIONIC EMITTERS, by C. B. Magee, M. J. Pool, W. D. McMullen, R. C. Jerner, and D. G. Ellis

47 pp. incl. figs.

First Annual Technical Summary Report, Nov. 1, 1961-Oct. 31, 1962 (NR 099-362)

Contract NONR-3361(01) Unclassified Report

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(over)

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1. Intermetallic Compounds
2. Beryllides
3. Thermodynamics
4. Thermionic Properties

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atom beryllium determined from these plots are: for Be, 79. 0; for $ZrBe_{13}$, 85. 0; for $NbBe_{12}$, 19. 9 and 59. 5; and for Nb_2Be_{17}, 98. 0 and 55. 8. That there are two enthalpies of sublimation for the niobium beryllides may possibly be due to the existence of a heretofore unknown niobium beryllide intermediate in beryllium content between Nb_2Be_{17} and $NbBe_3$. It is possible that both $NbBe_{12}$ and Nb_2Be_{17} decompose upon evaporation to the intermediate species which in turn decomposes to $NbBe_3$.

A high vacuum diode for the determination of the thermionic emission parameters of intermetallic compounds has been designed and constructed. A second diode incorporating many improvements over the first design is now being constructed. Fabrication of cylindrical emitter specimens of $ZrBe_{13}$ has been attempted by a number of techniques. Moderate success has been achieved only by cold pressing followed by sintering.

Apparatus for the determination of the compatibility of intermetallic compounds with cesium vapor has been designed and is now being constructed.

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